(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 678 945 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 95105817.1

(22) Date of filing: 19.04.95

(51) Int. Cl.[6]: H01S 3/19

(30) Priority: 20.04.94 JP 106055/94
20.04.94 JP 106056/94

(43) Date of publication of application:
25.10.95 Bulletin 95/43

(84) Designated Contracting States:
DE FR GB

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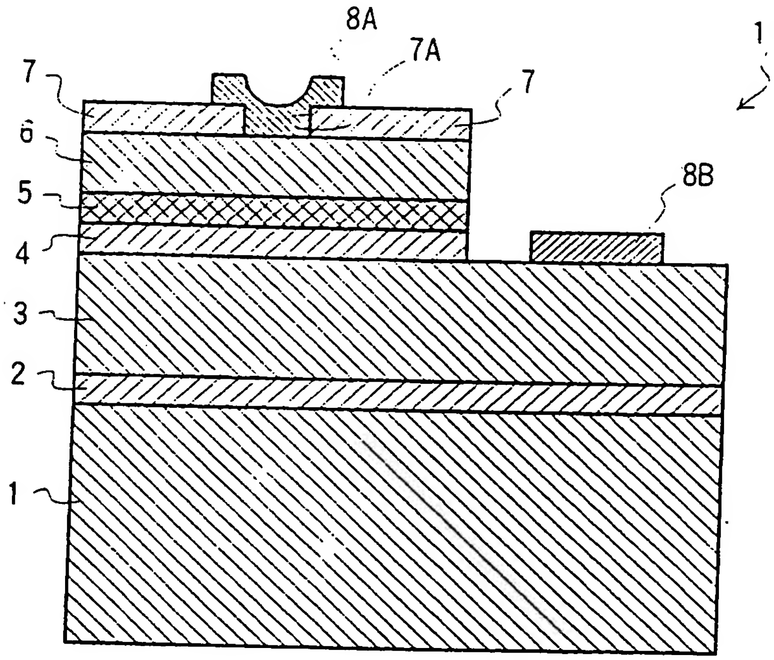
(54) Gallium nitride group compound semiconductor laser diode.

(57) A gallium nitride group compound semiconductor laser diode (10) satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$ is constituted by a double hetero-junction structure sandwiching an active layer (5) by layers (4, 6) having wider band gaps than the active layer (5). The active layer (5) is magnesium (Mg) doped p-type conductive gallium nitride group compound semiconductor satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$. In another embodiment, th active layer (5) is dop d with silicon (Si). As a result, luminous fficiency is improved and threshold current for oscillation is low red.

F I G. 1



BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a semiconductor laser diode (laser diode hereinafter) that emits visible short wave rays in the blue to violet and also in the ultraviolet region. Especially, the invention relates to a laser diode which requires less threshold current for oscillation.

Description of the Prior Art

A conventional laser diode disclosed in the United States Patent of 5,247,533 is constituted by a gallium nitride group compound semiconductor satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$ inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$, and its active layer is not doped with any impurities. Consequently, the laser diode has a problem of high threshold current for oscillation.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention to reduce the threshold current for oscillation.

According to the first aspect of the invention, there is provided a semiconductor laser diode satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$ comprising:

a double hetero-junction structure sandwiching an active layer by layers having wider band gaps than the active layer; and

wherein the active layer is magnesium (Mg) doped p-type conductive gallium nitride group compound semiconductor satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

According to the second aspect of the invention, the p-type conductive gallium nitride group compound semiconductor is obtained by one of electron irradiation, laser irradiation, heat treatment, and any combinations among the electron irradiation, the laser irradiation, and the heat treatment.

According to the third aspect of the invention, the p-type conductive gallium nitride group compound semiconductor is obtained by heat treatment in the atmosphere of nitrogen (N_2) gases under plasma state.

According to the fourth aspect of the invention, the active layer is constituted by silicon (Si) doped n-type conductive gallium nitride compound semiconductor satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$ inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

When the active layer is constituted by Mg-dop d GaN compound of p-type satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$ inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$, emission efficiency between bands is enhanced resulting in lowering threshold current for oscillation.

Further, when the active layer is constituted by Si-doped GaN compound of n-type satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$ inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$, emission efficiency of the active layer is improved resulting in lowering threshold current for oscillation.

Other objects, features, and characteristics of the present invention will become apparent upon consideration of the following description in the appended claims with reference to the accompanying drawings, all of which form a part of the specification, and wherein referenced numerals designate corresponding parts in the various figures.

BRIEF DESCRIPTION OF THE DRAWING

In the accompanying drawings:

FIG. 1 is a diagram showing the structure of the laser diode embodied in Example 1; and

FIG. 2 is a diagram showing the structure of the laser diode embodied in Example 2.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention will be more fully understood by reference to the following examples.

Example 1

FIG. 1 is a sectional view of a laser diode 10 with a sapphire substrate 1 embodied in Example 1.

The sapphire substrate 1 of single crystalline, whose main surface "c" (0001) was cleaned by an organic washing solvent and heat treatment, was placed on a susceptor in a reaction chamber for the MOVPE treatment. After the chamber is evacuated, the sapphire substrate 1 was etched at 1200 °C by a vapor of H_2 fed into the chamber under normal pressure. As a result, hydrocarbon group gases previously attached to the surface of the sapphire substrate 1 were removed to some extent.

About a 50 nm thick aluminum nitride (AlN) buffer layer 2 was epitaxially formed on the sapphire substrate 1 under conditions of lowering the temperature of the sapphire substrate 1 to 400 °C, keeping the temperature constant, and supplying trimethyl aluminum ($Al(CH_3)_3$) (TMA hereinafter) and ammonia (NH_3).

On the buffer layer 2, silicon (Si) doped GaN n^+-layer 3 of high carrier concentration was formed under conditions of raising the temperature of the sapphire substrate 1 to 1150 °C, stopping supplying only TMA, and additionally supplying trimethyl gallium ($Ga(CH_3)_3$) (TMG hereinafter), and

silane (SiH_4).

The wafer was taken out from the chamber so as to cover a portion of the GaN layer 3 as a mask with silicon oxide (SiO_2), and returned into the chamber. The chamber was evacuated again and supplied with hydrogen (H_2) and NH_3 raising the temperature of the sapphire substrate 1 to 1150 °C.

Then, about a 0.5 μm thick undoped $Al_{0.1}Ga_{0.9}N$n-layer 4 was formed on the portion of the n^+-layer 3 which was not covered with SiO_2 by supplying TMA and TMG.

About a 0.4 μm thick magnesium (Mg) doped GaN active layer 5 was formed on the n-layer 4 by supplying TMG and biscyclopentadienyl magnesium ($Mg(CH_5H_5)_2$) (CP_2Mg hereinafter).

About 0.5 μm thick Mg-doped $Al_{0.1}Ga_{0.9}N$ p-layer 6 was formed on the active layer 5 by supplying TMA, TMG, and CP_2Mg.

Then, the SiO_2 layer covering the portion of the n^+-layer 3 as a mask was removed by a hydrofluoric acid group etching liquid.

After a SiO_2 layer 7 was formed on the p-layer 6, a strip-like window 7A of 1 mm by 50 μm in dimensions was formed. Then, the wafer was transferred into a vacuum chamber, and electron rays were irradiated into the Mg-doped p-layer 6 and the Mg-doped active layer 5. This irradiation changed those layers 5 and 6 into p-type conductive lay rs.

Typical irradiation conditions are:

15 KV for the electron accelerating voltage;

120 μA for the emission current;

60 μmØ for the electron spot diameter;and

297 K for the sample temperature.

Subsequently, a metal electrode 8A was form d in the strip-like window 7A, and a metal electrode 8B on the GaN n^+-layer 3.

The obtained laser diode 10 was found to require 90 % lesser threshold current for oscillation than a conventional laser diode whose GaN active layer was not doped with any impurities.

Example 2

FIG. 2 is a sectional view exhibiting a structure of the semiconductor laser diode with a sapphire substrate in Example 2. A difference between Examples 1 and 2 resides in the active layer 5. In example 2, the active layer 5 is doped with silicon (Si), although the active layer 5 in Example 1 is doped with magnesium (Mg) and is irradiated with electron beams for p-type conduction. The manufacturing processes up to the AlGaN n-layer 4 was as same as those described in Example 1.

On the n-layer 4, about a 0.4 μm thick Si-doped GaN active layer 5 was formed by supplying TMG and SiH_4.

Subsequently, $Al_{0.1}Ga_{0.9}N$ p-layer 6 and metal electrodes 8A and 8B were formed by the same processes that were described in Example 1. The electron irradiation was carried out only onto the Mg-doped p-layer 6 at the same conditions those were described in Example 1.

The obtained laser diode 10 was found to require 90 % lesser threshold current for oscillation than a conventional laser diode whose GaN emission layer was not doped with any impurities.

Although sapphire was employed as the substrate in Examples 1 and 2, a silicon substrate, a 6H-SiC substrate, or a GaN substrate can be used, alternatively.

Further, one of electron irradiation, laser irradiation, heat treatment and any combinations among the electron irradiation, the laser irradiation, and the heat treatment can be used alternatively, although electron irradiation was employed for the p-type conductive layers 5 and 6 in Example 1 and for the p-layer 6 in Example 2.

Further, the p-type conductive layers were alternatively obtained by heat treatment in the atmosphere of nitrogen (N_2) gases under plasma state as described in the following processes.

The reaction chamber was evacuated, and then, N_2 gases were introduced there keeping the pressure of the chamber 100 Torr or less. After plasma discharge was carried out in the chamber at electric power of 10 to 100 W, heat treatment was carried out onto the substrate 2 for 5 to 60 min. keeping its temperature 500 to 900 °C. This discharge can be carried out with any one of high-frequency wave, microwave, direct current, and so on, alternatively. The substrate 2 was placed either in the state of plasma discharge that both of N radical species and ionized species existed or in the state of afterglow that only N radical species existed. The optimum conditions for the p-type conductive layers with fine crystallinity were 750 °C temperature of the sapphire substrate 1 and 40 W of electric power.

While the invention has been described in connection with what are presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiments, but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims.

A gallium nitride group compound semiconductor laser diode (10) satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$ is constituted by a double hetero-junction structure sandwiching an active layer (5) by layers (4, 6) having wider band gaps than the activ layer (5). The active layer (5) is magnesium (Mg) doped p-type conductive gallium nitrid group compound

semiconductor satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$. In another embodiment, the active layer (5) is doped with silicon (Si). As a result, luminous efficiency is improved and threshold current for oscillation is lowered.

Claims

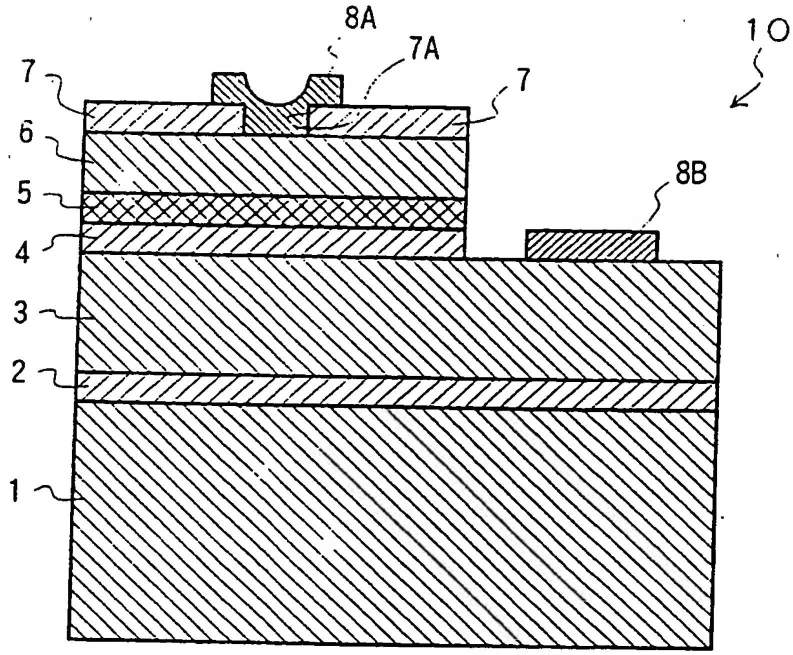
1. A gallium nitride group compound semiconductor laser diode (10) satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$ having a double hetero-junction structure sandwiching an active layer (5) by layers (4, 6) with wider band gaps than said active layer (5) is characterized in that said active layer (5) is magnesium (Mg) doped p-type conductive gallium nitride group compound semiconductor satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

2. A gallium nitride group compound semiconductor laser diode (10) satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$ of claim 1, wherein said p-type conductive gallium nitride group compound semiconductor is obtained by one of electron irradiation, laser irradiation, heat treatment, and any combinations among the electron irradiation, the laser irradiation, and the heat treatment.

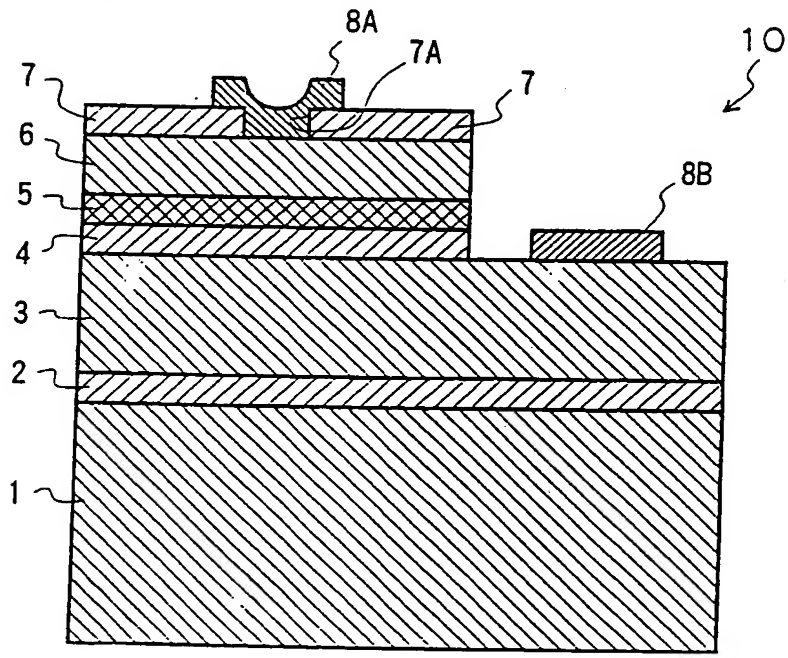
3. A gallium nitride group compound semiconductor laser diode (10) satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$ of claim 1, wherein said p-type conductive gallium nitride group compound semiconductor is obtained by heat treatment in the atmosphere of nitrogen (N_2) gases under plasma state.

4. A gallium nitride group compound semiconductor laser diode (10) satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$ having a double hetero-junction structure sandwiching an active layer (5) by layers (4, 6) with wider band gaps than said active layer (5) is characterized in that said active layer (5) is silicon (Si) doped n-type conductive gallium nitride group compound semiconductor satisfying the formula $(Al_xGa_{1-x})_yIn_{1-y}N$, inclusive of $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

F I G. 1



F I G. 2



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EUROPEAN SEARCH REPORT

Application Number
EP 95 10 5817

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	JAPANESE JOURNAL OF APPLIED PHYSICS PART 2, vol. 32, no. 7b, 15 July 1993 TOKYO JP, pages L1000-L1002, XP 000487415 H. AMANO ET AL 'Room temperature low threshold surface stimulated emission by optical pumping from AlGaN/GaN double heterostructure' * the whole document * ---	4 1	H01S3/19
D,A	US-A-5 247 533 (OKAZAKI NOBUO ET AL) 21 September 1993 * the whole document * ---	1-4	
A	OPTOELECTRONICS DEVICES AND TECHNOLOGIES, vol. 7, no. 1, 1 June 1992 pages 49-56, XP 000294314 ISAMU AKASAKI ET AL 'PERSPECTIVE OF THE UV/BLUE LIGHT EMITTING DEVICES BASED ON GAN AND RELATED COMPOUNDS' * the whole document * ---	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	JAPANESE JOURNAL OF APPLIED PHYSICS PART 2, vol. 31, no. 2b, 15 February 1992 TOKYO JP, pages L139-L142, S. NAKAMURA ET AL 'Thermal annealing effects on p-type Mg-doped GaN Films' * the whole document * ---	1-3	H01S
P,X	EP-A-0 599 224 (NICHIA CHEMICAL INDUSTRIES LTD) * the whole document * --- -/--	1-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	31 July 1995	Claessen, L

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
O : non-written disclosure
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P,X	PATENT ABSTRACTS OF JAPAN vol. 018 no. 673 (E-1647) ,19 December 1994 & JP-A-06 268259 (NICHIA CHEM IND LTD) 22 September 1994, * abstract * -----	1	
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& : member of the same patent family, corresponding document

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